ENVIRONMENTALLY SOUND VEGETAL FIBER–POLYMER MATRIX COMPOSITES

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The current work reviews the potential chemical modifications of vegetal fibers for future applications as reinforcement agents in new and environmentally sound organic matrix composites. Some considerations on the manufacturing processes of polymeric organic matrix composites are presented.

The chemical ways to improve interfacial linking between vegetal fibers and the polymeric matrix are evidenced, according to their importance. Different chemical treatments of vegetal fibers, favoring the development of interfacial bonding forces between composite components, are briefly discussed, together with some aspects on the environmental impact and life cycle of vegetal fiber composites, for evaluating the environmental impact of all products and services.

Keywords: vegetal fiber, cellulose, polymer matrix, environmentally friendly

INTRODUCTION

A composite material denotes a structure different from that of common heterogeneous materials. One of the most frequently cited definitions for composite materials has been provided by Gay *et al.*,[1] which states that the term "fiber composite material" refers to a material with strong, continuous or non-continuous fibers, surrounded by a weaker matrix material. The matrix distributes the fibers and transmits the load to the fibers.[1] The matrix materials used for the design and manufacturing of composites may be classified as: mineral matrix, which includes cement, gypsum and concrete mixture, silicon carbide and carbon; organic polymeric matrix, such as thermoplastic resins (polypropylene, polyphenylene sulfone, polyamide, polyetheretherketone, etc.) and thermoset resins (polyesters, phenolics, melamines, silicones, polyurethanes, epoxies); metallic matrix, as aluminum alloys, titanium alloys, oriented eutectics.

Man-made composites have been defined as materials made from one or more constituents with relatively different chemi-cal and physical properties, which remain rather distinct in the final product, and should override the properties of the individual constituents.[1] A classification of the possible sources of vegetal fibers for composite materials has been recently made by Gavrilescu *et al.*[2] Vegetal fiber reinforced materials have interesting applications in numerous fields, as in building products; transportation and automotive industry; for industrial and consumer goods. The uses of vegetal fibers in composite and non-composite materials are presented in Figure 1.

Over the last decade, there has been a continuous debate on the potential of integrating vegetal fibers into new and environmentally friendly composite materials. Vegetal fibers have an enormous potential of replacing the classical energy-intensive materials, considered responsible for the global climate change. The environmental friendliness of vegetal fibers resides in their economical advantages (low cost and low resource consumption for their production), renewability, low density,

recyclability, biodegradability and carbon sequestration, which recommend them as potential substitutes for glass fibers and other synthetic fibers in composite materials. The mechanical properties of vegetal fibers, especially of flax, hemp, jute and sisal, are very good and may compete with glass fiber as to specific strength and modulus.[3,4] Several widely cited drawbacks of using vegetal fibers in field applications may include: high level of moisture absorption capacity, dimensional instability – as a negative effect of water absorption, susceptibility to microbial attack and rotting, restricted processing temperature due to the low decomposition temperature of cellulose, insufficient adhesion to the polymer matrix and aging.[5] However, despite such disadvantages, vegetal fibers have been extensively investigated as possible substitutes for synthetic fibers used for the reinforcement of polymeric composites.[6]

Typical examples of vegetal fibers used for the production of composites include jute, hemp, cotton, kenaf and, last but not least, wood fibers[7] and wood pulp or recovered paper.[8] Both agricultural residues and recovered paper from cultivated plants have lately drawn the attention as potential new vegetal fiber resources. As an example, rapeseed plant residues and others may be here included.[4] Many of these fibers have low density, high toughness and acceptable specific strength and modulus. Moreover, the hollow cellular structure of some plant fibers provides good insulation against heat and noise.[9-13]

The present study reviews the potential chemical treatments for enhancing the interfacial link of vegetal fibers to the polymeric matrix in polymeric matrix composites. Some aspects on the environmental impact, by life cycle assessment (LCA) of the vegetal fiber composites, are also discussed, since LCA appears as the most frequently used procedure to evaluate the environmental impact of products.

Manufacturing of polymer matrix-vegetal fiber composites

Vegetal cellulosic fibers, renewable and abundantly available throughout the world, have been investigated for use as reinforcement agents in both thermoplastic and thermoset polymeric matrix composites. The difference between thermoplastic and thermoset polymer matrices is that, in the former, the molecules are joined together by weak intermolecular hydrogen forces or Van der Walls bonds, thus allowing heating and processing of the solid material according to the needs, while in the case of thermosets, the molecules are chemically bonded in a rigid three-dimensional network as a result of heat and pressure application during the curing phase.

As shown in Figure 1, the production of a vegetal fiber polymeric matrix involves several important stages. First, the fibers are selected and, if necessary, processed by physical, mechanical or chemical means. The polymeric matrix and the additives are selected according to the needs and are separately processed or conditioned. The incorporation of fibers into the polymeric matrix may result in two distinct categories: first, the fibers and the matrix are processed directly into the finished product or structure. Examples of such processes are filament winding and pultrusion, which are less used for vegetal fiber-polymer matrix composite production. In the second category, the fibers are incorporated into the matrix to obtain the so called ready-to-mold sheets, which can be stored and later processed to form laminated structures through autoclave molding or compression. These sheets are available as prepregs or sheet molding compounds. The additives usually used in the production of both categories may include inert fillers, pigments, UV stabilizers, catalysts, inhibitors and thickeners.[14]

Chemical and biochemical surface treatments of vegetal fibers

The application of vegetal fiber-polymer matrix composites has occurred at an industrial level.[15] It is generally agreed upon that the mechanical properties of vegetal fiber-reinforced polymers are largely determined by the characteristics of the fibers, polymeric matrices and by the interaction of the fiber-matrix interface. However, the main disadvantages of natural fibers in composites refer to the poor compatibility between fiber and matrix and the relatively high moisture sorption. According to literature,[16] the interfacial behavior between fibers and polymer matrices has been long recognized as a key factor influencing the overall properties of composite materials. Fiber-matrix interfacial phenomena control the stress transfer

between fiber and matrix, stress redistribution, as well as the mechanisms of damage accumulation and propagation. Bonding between fibers and the matrix occurs during the manufacturing phase of the composite material, influencing decisively the mechanical properties of the composite material. A better understanding of chemical bonding between vegetal fibers and the polymeric matrix is necessary for developing natural fiber-reinforced composites.

The components of vegetal fibers include cellulose, hemicellulose, lignin, pectin, waxes and water soluble substances.[2,3] It is a widely accepted idea that the interfacial linking between fibers and the polymeric matrix has low mechanical properties. This is a consequence of the improbability of chemical bonding between the polar hydroxyl groups of the fibers and the generally non-polar matrix. Chemical treatments of fibers may improve and optimize the interfacial linking by activating the hydroxyl groups and by introducing some new chemical moieties, which improve the link between the fiber and the polymeric matrix – as shown in Figure 3.

To achieve better interfacial properties, the so-called chemical coupling agents should accomplish two functions: to react first with the hydroxyl groups of cellulose and second, with the functional groups of the matrix.[2,16] Bledzki and Gassan[5] have proposed several coupling mechanisms in vegetal fiber composite materials: (1) elimination of the weak boundary layers; (2) generation of a stronger and flexible layer; (3) development of a highly crosslinked interphase region between that of the substrate and of the polymer; (4) improvement of wetting between the polymer and the vegetal cellulosic fiber; (5) formation of covalent bonds with both materials, and (6) alteration of substrate surface acidity.
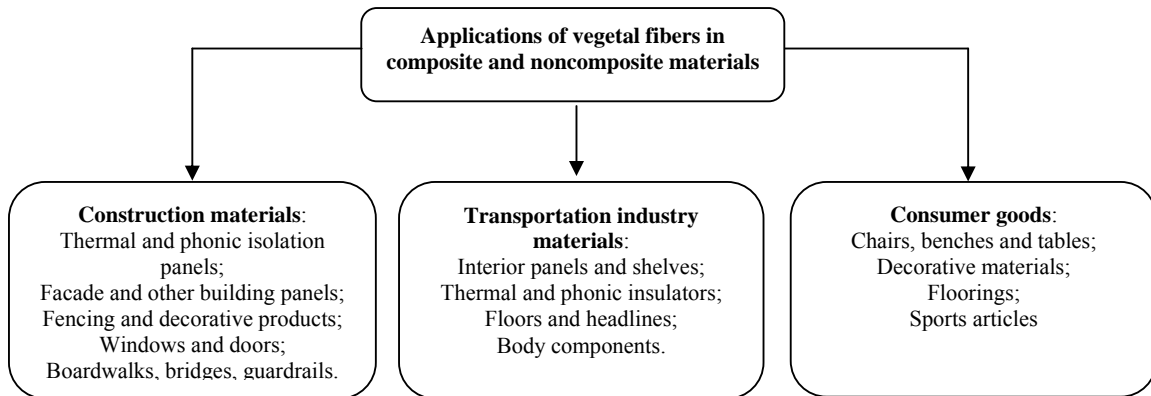
Figure 1: Synthetic presentation of possible applications of vegetal fiber-based composite materials
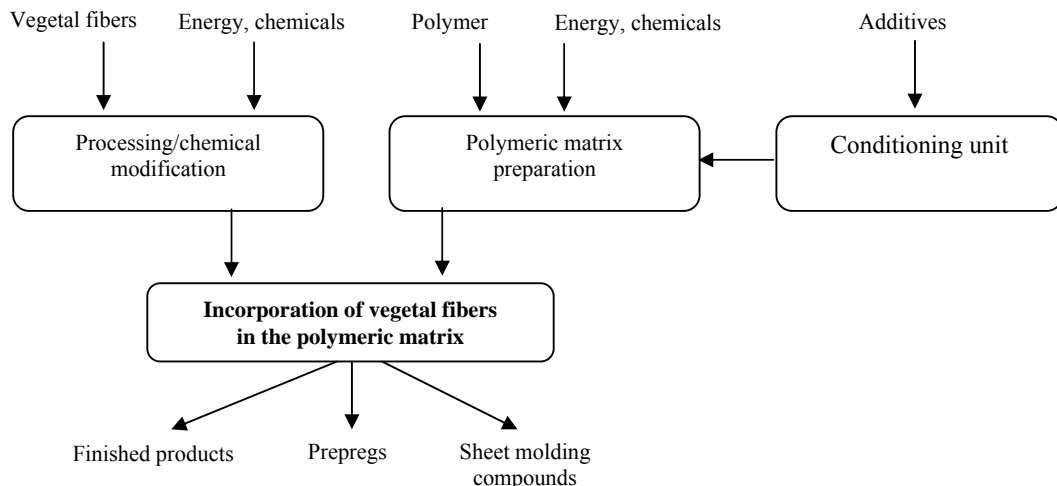
Figure 2: Schematization of vegetal fiber-polymeric matrix material manufacturing process
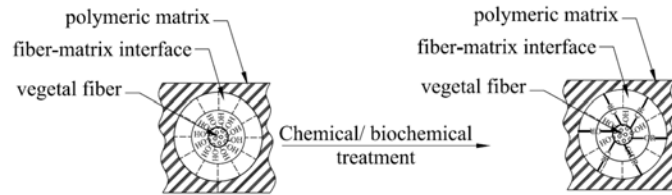
Figure 3: Principle of improving fiber-polymer matrix interfacial link by chemical treatment

Alkaline treatment

Alkaline treatment and mercerization are two of the most frequently applied chemical treatments for the reinforcement of vegetal cellulose fibers – thermoplastics and thermosets. An important modification induced by the alkaline treatment is the disruption of hydrogen bonding in the network structure, which increases surface roughness.[17] The treatment of vegetal fibers by aqueous sodium hydroxide (NaOH) promotes the ionization of the hydroxyl group to the alkoxide, as described by equation (1):

Vegetal fiber- OH + NaOH →

Vegetal fiber -O⁻Na⁺ + H₂O   (1)
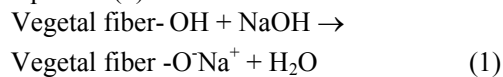
The alkaline treatments remove a certain amount of lignin and extractives, which cover the external surface of the fiber cell wall, dissolve hemicelluloses and, to some extent, may lead to cellulose depolymerization and exposure of short-length crystallites. Therefore, alkaline processing directly influences the vegetal fiber chemical composition.[18]

Mercerization of vegetal fibers involves immersion of the vegetal fibers into sodium hydroxide solutions for a given period of time. The duration of the treatment is variable, and the type of fibers, their purity in cellulose and the concentration of the used sodium hydroxide solution should be taken into account when establishing the duration of mercerization, to avoid irreversible fiber degradation. However, moderate- or short-time alkaline treatments have been reported to significantly improve the mechanical properties, impact fatigue and dynamic behavior of fiber-reinforced composites. Cao *et al.*,[19] who used different concentrations of NaOH solutions for the alkaline treatment of bagasse fibers, concluded that the utilization of a 1% NaOH solution for the treatment led to the best results as to the mechanical properties of composites. The improvement

was also the result of external fibrillation, which occurred during the alkaline treatment. An increased alkali concentration led to a loss of mechanical strength, as due to depolymerisation. Similar results were also obtained by a large number of authors, who used different types of vegetal fibers, sodium hydroxide concentrations and polymeric matrices.[20-24]

Esterification

Esterification is the generic name for a chemical reaction in which two reactants (typically, an alcohol and an acid) form an ester. Esters of cellulose with inorganic and organic acids were the first covalently modified cellulose derivatives to be synthesized in the laboratory. Cellulose nitrate, cellulose acetate and cellulose xanthate, produced at an industrial scale since the second half of the previous century, comprise today more than 90% of the production capacity in the chemical processing of cellulose.[17] Since the vegetal fibers contain a considerable amount of cellulose, esterification with organic acids are routes to be taken into consideration for improving fiber/matrix bonding and for reducing the water absorption capacity of the vegetal fiber-polymer matrix composites. The esterification of vegetal fibers may be performed by several chemical pathways, such as:

➢ reaction of vegetal fiber cellulose with organic acid anhydride;
➢ reaction of vegetal fiber cellulose with organic acid chloride;
➢ reaction of vegetal fiber cellulose with organic acid.

Acetylation of cellulose is one of the first discovered routes to obtain cellulosic derivatives. The results of the research on vegetal fiber composite production indicated an increased mechanical strength of the obtained biocomposites. Mishra *et al.*[24] have investigated the possibilities of acetylating

vegetal fibers (sisal fibers, equation 2) for increasing the mechanical properties of some vegetal fiber-polyester composites, by acetylating treatment with previous mercerization. Similar results were obtained[25, 26] on different types of vegetal fibers:

Vegetal fiber – OH + CH$_3$ – C(=O) – O – C(=O) – CH$_3$ $\longrightarrow$ Fiber – OCOCH$_3$ + CH$_3$COOH   (2)
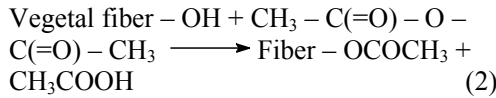
Benzoylation is another important transformation in organic synthesis and vegetal fiber treatment.[27] Benzoyl chloride is most often used in fiber treatment – see eq. (3) and Figure 4. Benzoyl chloride includes benzoyl (C$_6$H$_5$C=O), which is responsible for the reduced hydrophilic nature of the treated fiber and improved interaction with the hydrophobic polymeric matrix.

Benzoylation has also been found to contribute to the increase of the mechanical properties of vegetal fiber-polymer composites. The increase in mechanical strength (tensile and flexural properties) has been reported for vegetal fiber-reinforced composites with polystyrene matrix,[27] polyester resins,[28] high-density polyethylene (HDPE) and low-density polyethylene (LDPE), either individually or in mixture.[29]

Maleic anhydride (*cis*-butenedioic anhydride, toxilic anhydride, dihydro-2,5-dioxofuran), an organic compound with the formula C$_4$H$_2$O$_3$, is, in its pure state, a colorless or white solid with acrid odor. Maleic anhydride might be used as an esterification reagent for the free hydroxyl groups present on the surface of the vegetal fibers. Maleic anhydride easily hydrolyses to maleic acid, which is also used as a treatment agent. The main purpose of using maleic anhydride is to assure chemical bonding between the fiber and the polymeric matrix. To this end, maleic acid or maleic anhydride is first reacted with the polymeric matrix, to be chemically linked to it. In a secondary stage of the process, the modified polymeric matrix is reacted with the cellulose contained in the fiber, by formation of ester linkages with the free hydroxyl groups. The chemical process is described in Figure 5.

Positive results on the chemical bonding of polymer matrix to vegetal fibers by maleic acid or anhydride treatment were obtained by Elsabbagh *et al.*,[30] in the effort of manufacturing flax/polypropylene composites. Other results confirmed the possibility of increasing interfacial energy in the vegetal fibers-polymeric (other than polypropylene) composites; the mechanical properties, as well as their hydrophobic characteristics were also improved.[31-33]
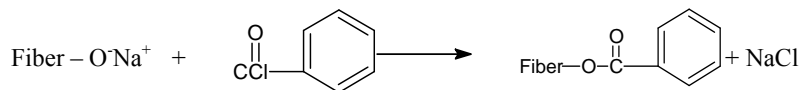

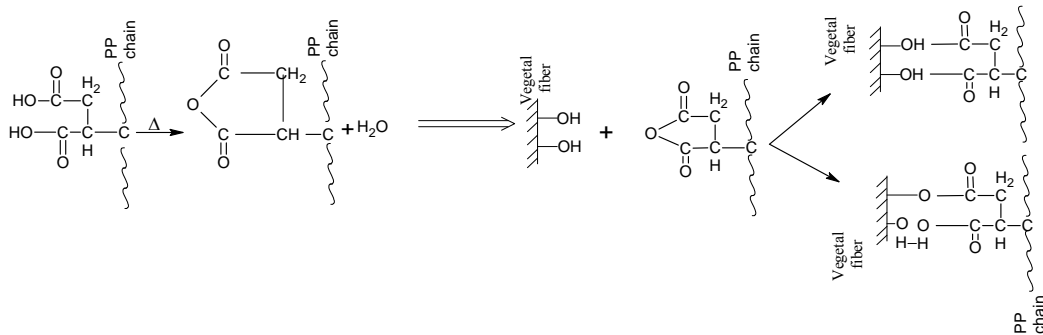Figure 4: Reaction of alkaline-treated fiber with benzoyl chloride

Figure 5: Stages in maleic acid/maleic anhydride polypropylene (PP) vegetal fiber chemical bonding
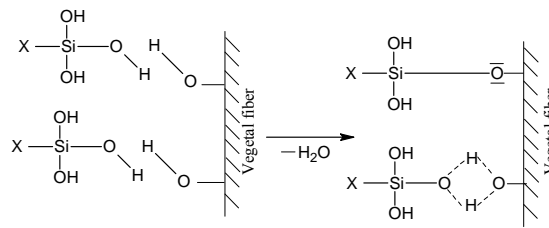
Figure 6: Reaction of silanols with hydroxyl groups from vegetal fiber surface

Silanization, that is covering of a surface through self-assembly with silane-like molecules, may reduce the number of cellulose hydroxyl groups in the fiber-matrix interface. Silanes (SiH_4) are used as coupling agents to let the glass fibers adhere to a polymer matrix, thus stabilizing the composite material. In the presence of moisture, the hydrolysable alkoxy groups lead to the formation of silanols. Silanol then reacts with the hydroxyl group of the fiber, forming stable covalent bonds to the cell wall, that are chemisorbed onto the fiber surface[34] – Figure 6.

The results on silane treatment mentioned in literature are somehow contradictory and do not always show improvement of the physical and mechanical properties of fibers. As an example, Naraprateep[35] has extensively studied the possibility of improving the physical properties of vegetal fiber-polypropylene composites. The silane treatment of the studied vegetal fibers (rosells and sisal) leads to improvements in tensile strength and Young's modulus, while water absorption decreased. Such improvements were the result of the fiber surface increase due to silane treatment, as revealed by SEM micrographs. Agrawal *et al*.[34] used silanisation to modify oil palm tree fibers and to obtain reinforced phenol formaldehyde composites. The obtained silanised fiber composites had higher thermal stability than the fiber composites alone.

Bamboo mated reinforced epoxy composites were fabricated by Kushwaha *et al*.,[36] who found out that the tensile strength of composites reinforced with only silane-treated fibers is comparable to that of composites with untreated fiber.

Graft polymerization

Graft polymerization is the process of obtaining a polymer containing molecules whose main backbone chain of atoms has, at various points, side chains attached to it, containing atoms or groups different from those in the main chain. The main chain may be a copolymer or it may be derived from a single monomer. Acrylic acid, acrylonitrile or styrene might be used for graft polymerization of cellulosic vegetal fibers. The acrylation reaction (Fig. 7) is initiated by the free radicals of the cellulose molecule. Acrylic acid treatment might be performed in non-polar solvents, in the presence of benzoyl peroxide.[37,38] Li *et al*.[39] improved tensile strength and lowered the water absorbtion capacity of flax fiber-HDPE composites after acrylic acid treatment of the above mentioned vegetal fibers.[39] Acrylonitrile is also a good candidate for graft polymerization (eq. 3) onto the surface of the vegetal fiber:

Vegetal fiber – $OH + CH_2 = CHCN \rightarrow$
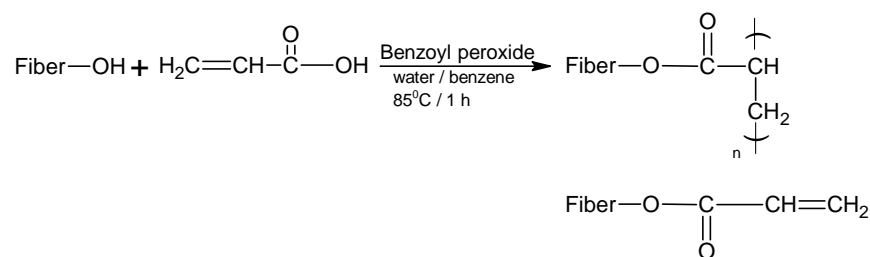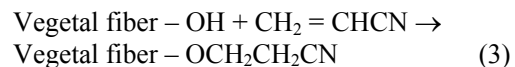Vegetal fiber – OCH_2CH_2CN (3)

Figure 7: Reaction of acrylic acid in the presence of benzoyl peroxide with hydroxyl groups from vegetal fiber surface
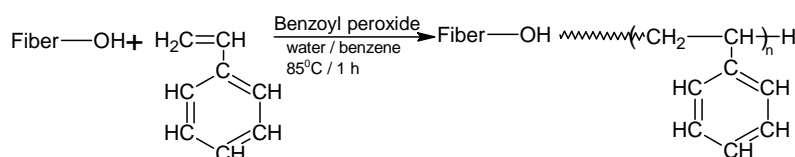
Figure 8: Reaction of styrene with hydroxyl groups from vegetal fiber surface

Beside the ceric salt catalyst, a combination of $CuSO_4$ and $NaIO_4$ might be used as initiator for the graft polymerization of acrylonitrile on the vegetal fiber surface. A decreased water absorption capacity was obtained by reducing the surface affinity to moisture. Mishra et al.[40] concluded that the decreased water absorption capacity was an effect of the orderly arrangement of the polyacrylonitrile units. A contradictory effect was obtained for tensile strength and Young's modulus tests: at 5% polyacrylonitrile grafting, these parameters were higher than at 10 and 25% grafting. Contradictory results – decreased mechanical and physical properties – have been obtained by Sreekala et al.[41] when attempting to use acrylonitrile-treated vegetal fibers as reinforcements for the production of phenol-formaldehyde resin composites. The styrene treatment of vegetal fibers (Fig. 8) and fiber surface graft polymerization led to the highest surface energy, a lower water absorption capacity and to a higher breaking strength of the polyester matrix-vegetal fiber composites.[41-43]

Other chemical treatments

Other chemical treatments include: peroxide treatment, permanganate treatment, sodium chlorite treatment, isocyanate treatment and stearic acid treatment.[3] Peroxide, permanganate and sodium chlorite treatment performed under different pH conditions and in aqueous or non-aqueous media generally removes some lignin and other fiber chemical constituents, such as hemicelluloses and extractibles. Oxidative treatments may also contribute to an increased number of carboxylic groups on the fiber surface.[3,44]

Synthetically, isocyanates are defined as compounds containing the functional isocyanate –N=C=O group, which is highly susceptible to react with the hydroxyl groups of cellulose, lignin and hemicellulose. Isocyanate is reported to work as a coupling agent used in fiber-reinforced composites.[3,45] Stearic acid treatment is less cited, but it has

been mentioned as a possible surface modification or coupling agent.[46] Some studies[47] indicate a possible reduction in fiber surface free energy and removal of the non-crystalline constituents.

The biochemical treatment of vegetal fibers is performed with commercially available enzymes or microorganisms. Such treatments are believed to improve the fiber matrix interfacial properties by either removing some fiber components or by introducing new ones. Some examples are provided in the following.

Li and Pickering[48] have employed white rot fungi (*Schizophyllum Commune*) for the treatment of previously chelated treated hemp fibers used in the production of polypropylene matrix composites. As a result of the white rot fungi action upon fibers, the mechanical properties of the composites were improved, following the removal of lignin, wax and hemicelluloses through the white rot fungi action. The removal of non-cellulosic compounds would also expose the hydroxyl groups on the fiber, and increase the potential for interaction between the hydroxyl sites and the coupling agent.

A fungal treatment with *Ophiostoma ulmi* obtained from elm tree infected with Dutch elm disease was preformed by Gulati and Sain.[49] After the treatment, the mechanical characteristics of the hemp-polyester composites obtained were improved, through improvement of the acid/base characteristics of the fiber surface and through higher resistance to moisture.

Pommet et al.[50] have studied the possible utilization of living microorganisms, such as *Acetobacter xylinium*, for depositing some bacterial cellulose onto the surface of vegetal fibers, thus increasing the strength of vegetal fiber–cellulose acetate butyrate and poly(L-lactic acid).

THE LCA OF VEGETAL FIBER-POLYMER MATRIX COMPOSITE MATERIALS

Life cycle assessment (LCA) of products is the most widely used method for

establishing the probable environmental impact of a given product or service. The most common definition of LCA refers to the investigation and evaluation of the environmental impacts of a given product or service caused or required by its existence. The goal of LCA is to assess and balance the possible impact of the product from its very beginning to its life end. There are several standardized LCA methodologies, most of them including the same phases: definition of goal and scope, inventory analysis, impact assessment and interpretation of results. The procedures of life cycle assessment (LCA) are part of the ISO 14000 environmental management standards: ISO 14040:2006 and 14044:2006. (ISO 14044 replacing earlier versions of ISO 14041 to ISO 14043).[51]

In the case of vegetal fiber composites, a simplified life cycle approach may be applied (Fig. 9). The green house gas emissions of the vegetal fibers are generally lower than those of artificial fibers.[2] However, additional information might be needed in the case of industrial crops, which may involve additional resources and energy consumption – to be measured and included

in LCA studies.[52,53] When agricultural wastes are used as sources of vegetal fibers, this issue should be carefully analyzed. Waste paper contains carbon, consequently, the recycling of these products keeps carbon sequestered.[54,55]

Manufacturing of composites is also an important life cycle stage. Processing of vegetal fiber to improve interfacial matrix bonding generally affects the *green image* of the obtained composites, because of the use of additional resources and energy consumption. It is generally agreed upon that natural fiber composites have a higher fiber content for equivalent performance, thus reducing even more the polluting base polymer content. Regarding the functional unit, the most often used is the mass weight of the material produced or the unit of product. Xu *et al.*[54] have introduced a new term: "material service density", which is defined as the volume of material satisfying a specific strength requirement. The rationale behind this is that specific volumes of different materials are required to withstand a given mechanical load.
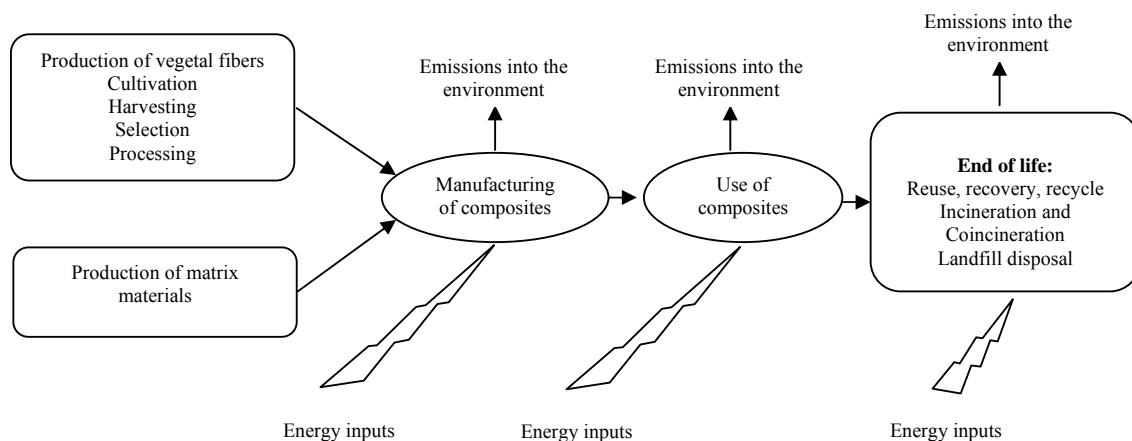

Figure 9: Simplified schematic approach to life cycle of vegetal fiber-reinforced composite materials

Energy inputs and environmental emissions may also occur during utilization. As an example, Joshi *et al.*[56] concluded the light-weight natural fiber composites improve fuel efficiency and reduce emissions in the usage phase of the component, especially in auto applications. The end-of-life of the product may require some energy for waste processing. Landfilling of automotive waste is generally not accepted by most of the EU countries, and the reuse, recycle or recovery is generally the widest

accepted end-of-life route.[57] Co-incineration of automotive waste vegetal fibers results in recovered energy and carbon credits.[58]

CONCLUSIONS

Sustainable development in the production of different materials means integration of natural and renewable resources into processes and products. Uses of vegetal fibers as potential reinforcement agents for composite materials are an adequate example for the above-mentioned

integration. The paper has described the main composite material applications for vegetal fiber sustainable integration into product.

Apart from the contribution of the vegetal fiber source, polymeric matrix, additives, manufacturing process, in the case of vegetal fiber-polymer matrix composites, it is generally agreed upon that the interfacial phenomena occurring between the vegetal fiber and the polymeric matrix play a key role in the composite properties. Several treatments in practice for improving the interfacial link between the vegetal fibers and the polymeric matrix are presented.

Vegetal fiber-based composites already employed in the production of different goods have been proven to have a lower environmental impact along the whole life cycle and better environmental compatibility, when compared to synthetic fiber-based composites. The use of vegetal fiber in composites also contributes to their carbon footprint reduction, due to atmospheric CO_2 consumption. Assessing the potential environmental impact by LCA studies of composites, produced by incorporating agricultural or waste paper products as vegetal fiber sources, may lead to better results compared to the use of cropped vegetal fiber sources. Chemical treatment procedures may negatively affect the results of LCA analysis.

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